

RELAXATION TIMES, MUTUAL AND AVERAGED MUTUAL VISCOSITIES OF SOME DI-SUBSTITUTED BENZENES IN SOLUTIONS OF CYCLOHEXANE

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ABSTRACT. Relaxation times of o-, m-, and p-nitro toluenes and o-chloro toluene have been determined in the 3 cms micro-wave region using cyclohexane as solvent at a temperature of 24°C. Mutual viscosities of the solute and solvent as proposed by Hill and averaged mutual viscosities as recently introduced by Vaughan and co-workers have also been determined in the solutions of cyclohexane. By differentiating the equations of Hill and Vaughan and coworkers with respect to the solute mole fraction two more equations have been obtained and the values of the mutual and averaged mutual viscosities obtained from these equations have been compared with those obtained directly from the equations of Hill and Vaughan and co-workers. It has been found that for the solutions studied the mutual viscosity coefficient is a better representation of the hindrance to the rotation of the individual solute molecules. The potential barrier heights for dielectric relaxation and viscous flow have also been calculated using Eyring's equations. The potential barrier height for dielectric relaxation is found to be always less than the potential barrier height for the viscous flow of the solvent.

INTRODUCTION

Hill (1954) suggested that the macroscopic viscosity of the solvent should be treated as the mutual viscosity of the solute and the solvent η_{12} , which is a measure of the solute-solvent interaction, in order to explain the discrepancy between the observed values of relaxation time (τ) and those obtained from Debye's equation. She gave the following expression for the mutual viscosity coefficient

$$\eta_m \sigma_m = x_1^2 \eta_1 \sigma_1 + x_2^2 \eta_2 \sigma_2 + 2x_1 x_2 \eta_{12} \sigma_{12} \quad \dots (1)$$

where η_m , η_1 and η_2 are the coefficients of viscosity of the solution, solvent and solute respectively. x_1 , x_2 are the mole fractions of the solvent and the solute and the quantities σ represent the average inter-molecular distances and are given by

$$\sigma_1 = (M_1/d_1 N)^{1/3}, \quad \sigma_2 = (M_2/d_2 N)^{1/3} \text{ and } \sigma_m = \left(\frac{x_1 M_1 + x_2 M_2}{d_m N} \right)^{1/3}$$

where M_1 , M_2 are the molecular weights of the solvent and solute respectively and d_1 , d_2 are the corresponding densities. d_m is the density of solution. σ_{12} represents the average separation of the solute and solvent molecules, i.e.

$$\sigma_{12} = 1/2(\sigma_1 + \sigma_2)$$

On rearrangement equation (1) yields

$$\left(\frac{\eta_m \sigma_m - x_1^2 \eta_1 \sigma_1}{x_2^2 \sigma_2} \right) = \eta_2 + 2 \frac{x_1}{x_2} \cdot \frac{\sigma_{12}}{\sigma_2} \cdot \eta_{12} \quad \dots (2)$$

This equation represents a straight line. The mutual viscosity η_{12} may be obtained from the slope of this line, drawn taking L.H.S. as ordinate and $2(x_1/x_2)(\sigma_{12}/\sigma_2)$ as abscissa as all the factors involved can be determined experimentally.

Assuming that $\sigma_m = \sigma_1$ and differentiating both the sides of equation (1) with respect to x_2 one gets

$$\frac{\sigma_1}{\sigma_2} \cdot \frac{1}{2x_2} \left(\frac{d\eta_m}{dx_2} - 2x_1 \eta_1 \right) = \eta_2 + \left(\frac{x_1 - x_2}{x_2} \right) \cdot \frac{\sigma_{12}}{\sigma_2} \cdot \eta_{12} \quad \dots (3)$$

This equation also represents a straight line and can similarly be used to determine η_{12} .

Meakins (1958) determined the mutual viscosity coefficients of large number of solutes in solutions of benzene and decalin and showed that the agreement between the experimental and calculated values of τ is much better in the case of Hill's equation of τ than that with Debye's equation. Later on Pitts and Smyth (1959) also showed from a similar observation that for the four systems observed by them, the value of τ obtained from Hill's equation are three to four times the corresponding experimental values of τ .

Recently Vaughan and co-workers (1961) derived on simple considerations an expression very similar to that of Hill, defining another mutual viscosity which they called the "properly averaged mutual viscosity". But they found no advantage of this viscosity over η_1 —the solvent viscosity, for the compound studied. Their equation in the present notation is :

$$\eta_m = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 \eta_{12} \quad \dots (4)$$

which yields on rearrangement

$$\left(\frac{\eta_m - x_1^2 \eta_1}{x_2^2} \right) = \eta_2 + 2 \cdot \frac{x_1}{x_2} \cdot \eta_{12} \quad \dots (5)$$

Differentiating both sides of equation (4) with respect to x_2 one gets

$$\frac{1}{2x_2} \left(\frac{d\eta_m}{dx_2} - 2x_1 \eta_1 \right) = \eta_2 + 2 \left(\frac{x_1 - x_2}{x_2} \right) \eta_{12} \quad \dots (6)$$

The equations (2), (3), (5) and (6) are equally good for a system in which the solute is in solid form, in that case η_2 represents an unknown factor. The equations (5) and (6) may be used to determine the "averaged mutual viscosities" η_{12} . In the present investigation the relaxation times (τ) of *o*-, *m*- and *p*-nitrotoluenes and *o*-chlorotoluene have been determined in 3 cms micro-wave region by Gopala

Krishna's (1957) fixed frequency method using cyclohexane as solvent. Mutual and averaged mutual viscosities of cyclohexane solutions of *o*-nitrotoluene, *m*-nitrotoluene, *o*-chlorotoluene and *o*-chloroaniline molecules have also been calculated from the slopes of the lines represented by equations (2), (3), (5) and (6) by the least square method. η_{12} for *p*-nitro toluene solutions was calculated from equation (5) by eliminating the factor η_2 from the two equations corresponding to two concentrations of the solute.

Potential barrier heights (H_7) for dielectric relaxation for the investigated compounds in solutions of cyclohexane and the potential barrier height (H_η) for the viscous flow of the solvent i.e. cyclohexane have been calculated using Eyring's (1941) equations.

EXPERIMENTAL

A 3 cms microwave bench was used for the determination of the dielectric constant, ϵ' and the loss factor ϵ'' of the dilute solutions of increasing concentrations, by the standing wave technique of von Hippel and Roberts (1946). Micro waves were generated by a reflex klystron (CV129). After travelling through a system of wave guides these waves were reflected from a short circuit at the end of a silver cell and standing waves were formed in the waveguide as a result of interference of the incident and reflected waves. The position of any minima of these standing waves, with and without the experimental solution in the cell were determined. This gave the shift of the minimum field position. The width at double the minimum field was also determined for each solution. The shift of the minima and the width at double the minimum field were used to calculate the dielectric constant ϵ' and dielectric loss factor ϵ'' of the solutions. Dakin and Works' (1947) simplified method for the calculations of ϵ' and ϵ'' was used in the case of solutions of *o*-nitrotoluene, *m*-nitrotoluene and *o*-chlorotoluene as the dissipation factor was always found to be less than 0.1. Finally the relaxation times τ were calculated using Gopala Krishna's (1957) relation. The viscosities were determined with the help of Hoppler's precision viscometer to an accuracy of $\pm 2\%$. This method of determining viscosity is very simple and requires simply the determination of time of fall of a glass or metal ball between two marks in a glass tube filled with the experimental liquid of known density. The viscosities (η cps) of the liquids were calculated from the relation :

$$\eta = F(S_k - S_F) \cdot K$$

where

F = time of fall of the ball in seconds,

S_k = specific gravity of the ball,

S_F = specific gravity of the liquid,

K (ball constant) = 0.009495

It was observed that if an error of 1% is made in any experimental measurement,

the maximum extent to which η_{12} is affected is about 1.6%. The chemicals used were of pure quality and were obtained from Messrs E. Merck, B.D.H. and Light. Cyclohexane used as solvent was of B.D.H. LR grade and was distilled before use.

DISCUSSION OF THE RESULTS

The graphs given in the Figs. 1 and 2 represent the values of the factors X Y calculated from the dielectric constants ϵ' and the dielectric loss factors ϵ'' , for solutions of increasing concentrations of each solute studied. The slopes of these lines, required in the calculations of relaxation times (τ) were determined by the least square method. The values of relaxation time τ , the average mutual viscosities η_{12} and the ratios τ/η_1 and τ/η_{12} together with the corresponding values of molecular weight for each compound are given in Table I. The results show that the relaxation times of the three nitro-toluenes increase from ortho- via meta- to para-compound. The ratios τ/η_1 for these compounds are different from each other and also increase in the same order. This is not in conformity with the Debye's theory (1929). But if η_1 —the solvent viscosity is replaced by η_{12} —the averaged mutual viscosity of the solute and solvent as in the last column of Table I, the difference between the ratio (τ/η_{12}) for the three nitrotoluenes becomes much

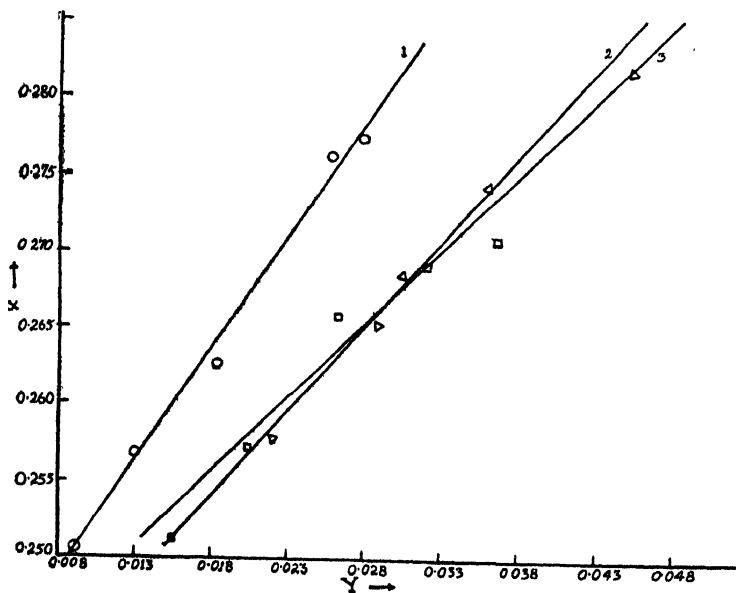
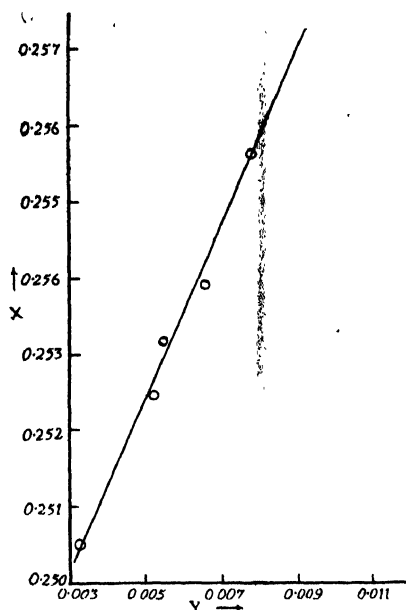


Fig. 1. Plot of X-Y data for :

1. o-nitro-toluene.
2. m-nitro-toluene.
3. p-nitro-toluene.

Fig. 2. Plot of X-Y data for *o*-chloro toluene.

less than with η_1 . The ratios for *m*- and *p*-nitro toluenes are found to be almost equal. Therefore in these cases η_{12} seems to be a better representation of the resistance to the rotation of individual solute molecules. From the results it is evident that the relaxation times of three nitro-toluenes increase from ortho- via meta- to para-compound because the resistance experienced by a nitro-toluene molecule, also increases in the same order. The results also show that the values of τ , (τ/η_1) and (τ/η_{12}) for *o*-nitro-toluene which has greater molecular weight are greater than those for *o*-chlorotoluene as expected. But the difference between the (τ/η_{12}) values for these molecules is less than that between the values of (τ/η_1) for the same molecules. This is due to the fact that the resistance experienced by a *o*-nitro toluene molecule in rotation is greater than that experience by a *o*-chloro-toluene molecule as can be seen from the values of η_{12} for the solutions of these compounds.

The Table II contains the values of the viscosity co-efficients η_{12} as determined from the equations (2), (3), (5) and (6) for four compounds. The values of the averaged mutual viscosity for different solutions as determined from the equation of Vaughan and co-workers (1961) i.e. equation (5) are almost equal to those of the corresponding mutual viscosities determined from the equation (2) of Hill (1954) except in the case of *o*-chloro toluene where the difference is slightly more than that in the case of other compounds. This is in agreement with the results obtained earlier by Vaughan and co-workers (1961) in the case of some other polar molecules. In the 4th and 5th columns of the Table II, are given

respectively the values of η_{12} as obtained from equation (3) of Hill and equation (6) of Vaughan and co-workers. It is found that the corresponding values of η_{12} in the two columns are approximately equal, but they are slightly different respectively from the values of η_{12} obtained from the corresponding equations (2) and (5) and given respectively in the 2nd and 3rd columns, the difference being comparatively larger in the case of *o*-chloro aniline.

In the Table III are listed the values of the potential barrier heights for dielectric relaxation (H_τ) for the polar disubstituted benzenes studied and the potential barrier height (H_η) for viscous flow of the solvent calculated from the Eyring's equations, together with the corresponding values of relaxation time. In these calculations the Eyring's value of the constant A i.e. $(k/h) = 4.8 \times 10^{-11}$ and that of the constant $B = (hN/V)$ (where h = Planck's constant, K = Boltzmann constant, N = Avogadro's number and V = molar volume), were used. A study of the Table III shows that the potential barrier heights H_τ are slightly different for different molecules. The values of H_τ for the three nitro toluenes which have the same size, are found to be slightly different, probably because a constant value of A has been used in all the cases while it has been shown by Sobhanadri (1959)

TABLE I

Values of relaxation times (τ), averaged mutual viscosity (η_{12}) and the ratios (τ/η_1), (τ/η_{12}) for the investigated compounds
($f = 9567$ MC/Sec. Viscosity of cyclohexane at $24^\circ\text{C} = 0.9754$ cps)

Substance	Molecular Weight	$\tau \times 10$ sec.	$\tau/\eta_1 \times 10$	η_{12} cps.	$\tau/\eta_{12} \times 10$
<i>o</i> -nitro toluene	137.13	10.9	11.18	1.142	9.54
<i>m</i> -nitro toluene	137.13	15.1	15.48	1.350	11.19
<i>p</i> -nitro toluene	137.13	18.8	19.27	1.668	11.27
<i>o</i> -chloro toluene	126.58	10.0	10.25	1.080	9.26

TABLE II

Values of mutual viscosities (η_{12}) as determined from different equations

Substance	η_{12} cps from			
	Eqn.(2)	Eqn.(5)	Eqn.(3)	Eqn.(6)
<i>o</i> -nitro toluene	1.165	1.142	1.049	1.064
<i>m</i> -nitro toluene	1.365	1.350	1.089	1.103
<i>o</i> -chloro toluene	1.041	1.080	1.009	1.021
<i>o</i> -chloro aniline	0.943	0.954	1.427	1.427

TABLE III

Values of relaxation time (τ) and the potential barrier heights for dielectric relaxation and viscous flow

Substance	$\tau \times 10^{12}$ Sec	H_τ (K cal/mole)	H_η (K cal/mole)	H_η/H_τ
o-nitro toluene	10.9	2.49	3.30	1.33
m-nitro toluene	15.1	2.68	3.30	1.23
p-nitro toluene	18.8	2.81	3.30	1.17
o-chloro toluene	10.0	2.44	3.30	1.35

and Bhanumati (1963), that 'A' has different values for different solutes. The barrier heights H_τ are definitely less than H_η , the ratio of H_η and H_τ being as 1.35. This result is in conformity with the view of Franklin *et al* (1950). They determined the activation energies H_τ of *n*-octyl bromide in heptane, cyclohexane and hexadecane and found that H_τ is nearly equal to H_η only in Heptane which has slightly lower viscosity. The potential barrier height H_η is always higher than H_τ , because while in the process of viscous flow both rotation and translation are involved, the process of dipole orientation involves only rotation.

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